THE ADSORPTION OF CARBON MONOXIDE ON PLATINUM AND RHODIUM ELECTRODES

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INTRODUCTION

The adsorption of carbon monoxide on noble metal electrodes is of current interest in connection with several areas in the field of fuel cell technology. These areas include anodic oxidation of CO (7), of impure hydrogen containing CO (8), and of organic substances where adsorbed CO is suspected of being an intermediate (9). In this paper, the author will compare the results of earlier (1-4) studies of CO adsorption on Pt with more recent observations (5) made on the adsorption of CO on Rh under roughly similar experimental conditions.

EXPERIMENTAL

The original papers (1-5) may be consulted for experimental details. The Pt and Rh electrodes were smooth polycrystalline wires. Pt wires were generally annealed in a hydrogen flame. Rh electrodes were annealed near the melting point in a high-vacuum bell jar. Both metals were sealed into soft glass supports at one end, using a cool hydrogen flame. The surfaces were given a light etch in aqua regia.

All potentials are referred to a reversible hydrogen electrode immersed in the same solution as the working electrode.

All values of charge and current density are reported on the basis of the <u>geometric</u> area, unless otherwise specified.

DISCUSSION

Hydrogen and Oxygen Adsorption on Clean Pt and Rh Electrodes-

Numerous voltametric studies have been made of the adsorption of hydrogen and "oxygen" (including possible formation of oxides or oxide precursers) on Pt and Rh electrodes, and the results have been reviewed by several authors (10-15). The following qualitative conclusions for sulfuric or perchloric acid electrolyte are useful in establishing proper conditions for the study of CO adsorption and in interpreting the results:

1) The coverage of both Pt and Rh electrodes with hydrogen atoms approaches a monolayer near 0 v.. The coverage gradually decreases to zero at 0.3 - 0.4 v. (depending on temperature) for Pt and at 0.1 - 0.2 v. for Rh. The adsorption and desorption of hydrogen atoms possesses a high degree of reversibility for both metals.

2) The adsorption of "oxygen" begins at potentials below ca. 0.8 v. for Pt and below ca. 0.6 v. for Rh. The "adsorption" is not reversible (except possibly at very low coverages) insofar as the dissolution of the "oxygen" film occurs at potentials several tenths of a volt less anodic than the formation.

Steady-State Oxidation of CO and H_2-

Information on the steady-state oxidation of CO and H_2 on Pt and Rh electrodes provides information useful in interpretation of results of adsorption studies. "Polarization curves" obtained in stirred sulfuric acid appear in Fig. 1. The curves were obtained under the conditions of a slow linear sweep but similar results may be obtained point-by-point at constant potential. For hydrogen on both Pt and Rh, (Fig. 1a and 1b), transport-controlled oxidation is observed slightly above the reversible potential. Onset of passivation of the oxidation is apparent at the potential of oxygen adsorption (above ca. 0.6 and 0.8 v. for Rh and Pt, respectively), and is almost complete within a few additional tenths of a volt. For CO, a flat limiting current is not observed, since initial CO oxidation and initial passivation almost coincide. The steep initial rise in CO oxidation current has previously been ascribed, for Pt (3), to a reversal of "self poisoning". A similar interpretation seems likely for Rh as well. Compared with hydrogen, the passivation of CO oxidation occurs over a wider range of potentials, particularly for the Pt electrode.

Electrode Pretreatment-

A convenient initial condition for the study of adsorption is that for which the surface coverage with the adsorbate (and with impurities) is initially zero and no reaction occurs between the surface and the adsorbate (hence the concentration of adsorbate near the electrode surface is same as that in the bulk of the solution). For some adsorbates (e. g., some ions and hydrocarbons) this condition may be achieved at some potential with the Pt surface in the reduced state. For CO on Pt and Rh, this condition may only be achieved by passivating the surface with an "oxygen" film. For Pt (sequence of Fig. 2a) a potential as high as approximately 1.8v. (step A) is required, not only for sufficient passivation, but also to remove such refractory impurities as the hydrocarbons (16). Products of the anodization (CO_2, O_2) may be eliminated at some lower potential (e. g., step B) at which the "oxygen" film is still retained. Rapid reduction of the surface and subsequent adsorption occurs during step C. For Rh (sequence of Fig. 2b) the high-potential anodization of step B eliminates all refractory adsorbed substances, but the resulting "oxygen" film is reduced very slowly (as compared with Pt). After this more rigorous cleanup, the anodization of the surface at 1.2 v. (step D) is sufficient for Rh (unlike Pt) to strip off CO_2 and fully passivate the surface against CO re-adsorption or oxidation.

In Fig. 2a, trace A is believed to correspond to the clean Pt surface. Variations such as traces B and C are believed (2,6) to correspond to a surface contaminated by electrolyte impurities since such variations are accellerated by stirring and retarded by solution purification procedures. Similar observations have been made by Giner (17) and Brummer (18) for Pt in sulfuric and phosphoric acids, respectively. The situation for Rh (Fig. 2b) appears similar to that for Pt, with trace 1 corresponding to the clean surface and traces 2 and 3 corresponding to surface contamination.

Determination of CO Coverage by Anodic Stripping-

In the potential sequence of Fig. 3a, the Pt surface is pretreated as discussed above. The surface is them reduced during the first few milliseconds of step C, and CO adsorbs on the freshly reduced surface. Application of sweep D results in the current-time (potential) traces. Trace A of Fig. 3a corresponds to zero coverage with CO and the charge (area) obtained by integrating under the

curve starting at the potential of steeply-rising current corresponds to oxidation of the surface, charging of the ionic double layer and (at higher potentials) to evolution of molecular oxygen. Traces B-F correspond to increasing coverage of the surface with CO and compared with trace A, additional charge flows corresponding to oxidation of adsorbed CO to CO_2. Using trace F as example, we see that this trace merges with that for the clean surface at time t_1 (or potential E_1). This suggests that despite initial conditions, the two surfaces are in the same state by time t_1. This in turn, suggests (2) that, (in spite of the other coulombic processes occurring) ΔQ, the difference in charge under traces F and A may correspond almost exactly to Q_{CO}, the charge required to oxidize adsorbed CO to CO_2. This assumes that the sweep is sufficiently fast that diffusion and subsequent oxidation of CO <u>during</u> the sweep is negligible. In this case:

$$\Delta Q = Q_{CO} = 2F\Gamma_{CO} \tag{1}$$

Where Γ_{CO} is the coverage of the surface with CO in moles per cm^2. The experimental observations (1,2) tend to support the validity of equation (1) for Pt. First, ΔQ is found to remain constant throughout a range of sweep speeds where errors due to diffusion of CO during the sweep are not anticipated. Second, the adsorption rate determined through anodic stripping obeys a calculated diffusion rate law to within 10% (2). Galvanostatic transients may also be used in determining the CO surface coverage (19-22) in a manner similar to the use of a linear sweep. Variations between investigators in reported maximum coverage are likely due in part to the details of correcting for oxidation of the surface (4).

Equation (1) seems to apply for Rh as well as for Pt (5). In the sequence of Fig. 3b, rapid reduction of the surface occurs during step F, but the major part of the adsorption may be allowed to occur at any other potential U (during step G). Step H is applied to eliminate "oxygen" adsorbed at larger values of U. Sweep I is applied to sample the extent of adsorption and the current-time (potential) traces obtained are similar to those obtained for Pt. As for Pt, ΔQ is relatively independent of sweep speed and the experimental adsorption rate follows a good linear diffusion law (5), until high coverages are achieved.

Kinetics of CO Adsorption-

Until the coverage exceeds at least 75% of the maximum, the kinetics of CO adsorption on both Pt and Rh is sufficiently rapid that transport control is observed in both quiescent and mechanically stirred solutions (2,4,5). This applies for potentials ranging from that of hydrogen gas evolution to that of anodic attack on CO.

Effect of Potential on the Structure of the Adsorbed Layer-

Carbon monoxide adsorbs on both Pt and Rh electrodes over a range of potentials extending from highly reducing to highly oxidizing conditions. It is reasonable to suspect therefore, that the adlayer may vary in composition or structure corresponding to partial oxidation or reduction of the original adsorbate. During a linear anodic sweep, there are coulombic processes in addition to the oxidation of CO and the situation is therefore kinetically complex. Nevertheless, the linear anodic sweep trace may be used to characterize the adlayer, if comparisons are made under carefully controlled conditions. In Fig. 4a and 4b, using the results for U=0.12 v. as the bases for comparison, traces for CO on Rh are compared from -0.2 v. to 0.5 v.. When the traces are compared at (approximately) equal values of Q_{CO}, the results are almost identical over this entire range of potentials. For Pt (Fig. 4c) at full

coverage the identical trace (trace 2) is obtained for potentials from -0.1 to
0.7 v.. Trace 3 is obtained at -0.2 v. and may correspond to partial
reduction of the adlayer. Excluding potentials as low as -0.2 v. for Pt,
it may therefore be concluded that there is no evidence for structural
variations in the CO adlayer on either Pt or Rh over most of the range of
potentials at which CO adsorbs.

Steady-State Coverage with CO-

Fig. 5 presents the fractional coverage of a Pt electrode surface with
CO as determined under the conditions of a slow triangular sweep. Very
similar results may be obtained on a point-by-point basis at constant potential.
The decreased coverages observed during part of the descending sweep is due
to the lag in reduction of the "oxygen" film formed at high potentials (1).
For a hypothetical perfectly smooth electrode, the maximum value of $Q_{CO}=$
0.28 mcoul./cm^2 (4) (based on the hydrogen area) corresponds to $\Gamma_{CO}=1.4 \times 10^{-9}$
moles/cm^2 (based on the hydrogen area) with ca. 90% of the available (hydrogen)
sites occupied by CO. This maxumum value remains constant for CO partial
pressures over a range of at least 0.01 to 1 atmosphere (4).
      The results for Rh (fig. 6) were obtained at constant potential. As
for Pt, we see that a flat maxumum is obtained for a wide range of potentials
and CO partial pressures. The maxumum value of Q_{CO} as calculated for a smooth
surface is 0.44 mcoul./cm^2 (hydrogen area), equivalent to $\Gamma_{CO}=2.2 \times 10^{-9}$
moles/cm^2 (hydrogen area). This corresponds to almost complete coverage of
available (hydrogen) sites with CO.
      For both Pt and Rh the coverage with CO tends to fall off precipitously
at the same potentials where CO is oxidized to CO_2, and where there is also
the onset of "oxygen" adsorption for both Pt and Rh. For Rh as for Pt (15)
it may be argued that the explanation most attractive at present, is that the
adsorption of "oxygen" causes the rate of adsorption to become activation-
controlled and sufficiently slow that it is overwhelmed by the rate of CO
oxidation. This causes the surface coverage to drop down to a very small value
(experimentally indistinguishable from zero). The decrease in surface coverage
with CO is, in turn, largely responsible for the initial decrease in anodic
corrent at high potentials (Fig. 1c and 1d).

Hydrogen Co-deposition Measurements and Structure of the Adlayer-

If a cathodic sweep is applied to a Pt or Rh electrode partially covered
with CO (and in the absence of previously adsorbed hydrogen or "oxygen"),
the major coulombic process will correspond to the deposition of hydrogen atoms
on sites not previously blocked by CO (2,5). Fig. 7a and 7b are some typical
traces obtained for Pt and Rh, and Fig. 7b demonstrates the construction
lines that may be drawn to define a closedarea (charge), $_SQ_H$ corresponding to
hydrogen codeposition. These construction lines serve mainly to differentiate
between the end of the hydrogen adsorption and the onset of the molecular
hydrogen evolution processes. It is to be noted that the implicit assumption
involved is that appreciable molecular hydrogen evolution does not begin until
the mixed monolayer is largely complete. The sweep is continued to any value
of the potential required to force the hydrogen evolution process at the
particular coverage with CO. The greater irreversibility of hydrogen adsorp-
tion on Rh is evidenced by the much higher overpotentials required at the
particular sweep speed employed.
      Subject to the limitations in evaluating $_SQ_H$, the following relationship
may hold for either Pt or Rh:

$$_S Q_H = F \cdot {}_S\Gamma_H = F[({}_S\Gamma_H)_o - m\Gamma_{CO}] \qquad (2)$$

where ${}_S\Gamma_H$ saturation coverage of the surface with hydrogen atoms in the presence of adsorbed CO

$({}_S\Gamma_H)$ =saturation coverage of the surface with hydrogen atoms in the absence of adsorbed CO

m=average number of hydrogen adsorption sites obscured per molecule of CO adsorbed.

For (2) to apply it is only necessary that no desorption of CO occur during the sweep, as may be verified experimentally. If we further assume that CO and hydrogen adsorption sites are similar and that hydrogen adsorption may only be blocked directly by formation of a CO - surface valence bond, then m may have the significance of representing the number of valences formed between a CO molecule and the surface. For CO on Pt at 30°C (2), m was found to have the value 2 for the first 30% of coverage, and 1 for the remainder [suggesting "bridged and "linear" structures (23) respectively]. The apparent bridging decreased at 60°C. For Rh at 80°C, only the one-site adsorption was suggested by the observed value of m=1, determined from the plot of Fig. 8(5). As for Pt, a two-site adsorption might be indicated at lower temperatures.

The Hydrogen-Adsorption Isotherm-

In somewhat different experiments to those discussed above, hydrogen atoms may be adsorbed at constant potential on a surface partially covered with a measured amount of CO. The coverage with hydrogen may then be determined by selective anodic stripping with a linear anodic sweep (5). The charge-potential plot of Fig. 9 is essentially an adsorption isotherm (since fractional coverage is proportional to the charge and the logarithm of hydrogen partial pressure is proportional to the potential) for the clean Rh surface, similar to those previously reported by Will and Knorr (24) and by Bold and Breiter (25). Fig. 10 reveals how the coverage with hydrogen at constant potential decreases linearly with increasing CO adsorption time. The CO surface coverage is increasing linearly under these conditions, and analysis of the plots reveal that the following empirical relationship exists at all potentials, between fractional hydrogen and CO surface coverages (below 80% of full coverage with CO):

$$\theta_H = (\theta_H)_o [1 - \frac{\theta_{CO}}{1.4}] \qquad (3)$$

where θ_H=fractional coverage with hydrogen atoms=$Q_H/{}_S Q_H$

$(\theta_H)_o = \theta_H$ in absence of adsorbed CO

θ_{CO}=fractional coverage with CO=$Q_{CO}/(Q_{CO})_{maximum}$

Expression (3) implies that the <u>shape</u> of the adsorption isotherm for the clean surface is retained as CO adsorbs. The resulting implication is that there is a random distribution of CO molecules on hydrogen adsorption sites possessing different heats of adsorption. This contrasts with the conclusion of Breiter (22) for formic acid adsorption on Pt. According to Breiter, initial adsorption of formic acid on Pt occurs on those sites having the highest heats of adsorption for hydrogen atoms.

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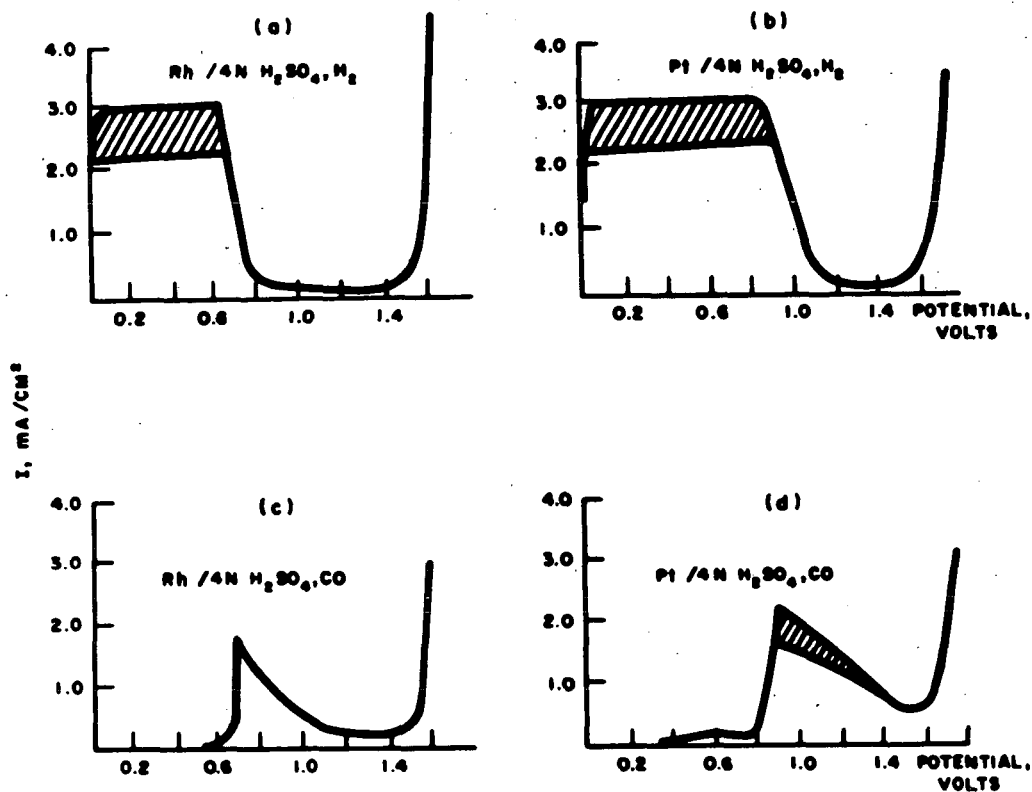25. W. Böld and M. Breiter, Z. Elektrochem. 64, 897 (1960).

Figure 1. Polarization curves measured for smooth Pt and Rh electrodes during application of a linear anodic sweep of speed 0.04 v. sec. The electrolyte was saturated with the gas at either 30°C (Pt electrode) or 80°C (Rh electrode) and the solution was paddle-stirred (300 rpm) throughout the experiment. The hatched areas correspond to regions of oscillation of the current. (From Ref. 5)
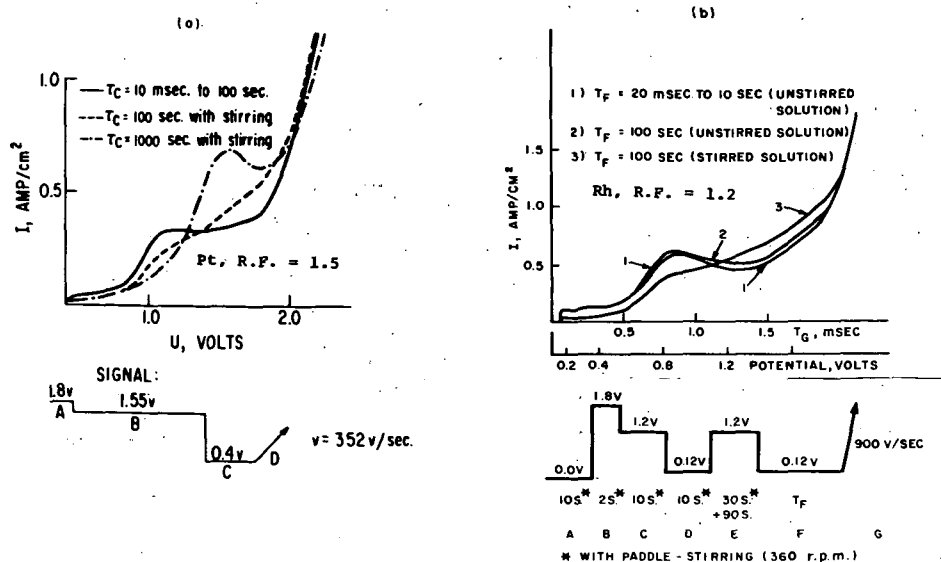
Figure 2. Adsorption of electrolyte impurities by smooth Pt and Rh electrodes. In Figure 2a, steps A and B are for pretreatment, adsorption occurs during step C (0.4 v., 1 N HClO$_4$ 30°C) and the traces are recorded during sweep D. In Figure 2b, steps A-E are for pretreatment, adsorption occurs during step F (0.12 v., 4 N H$_2$SO$_4$ 80°C) and the traces are recorded during sweep G. (Figure 2a from Ref. 6; Figure 2b from Ref. 5).
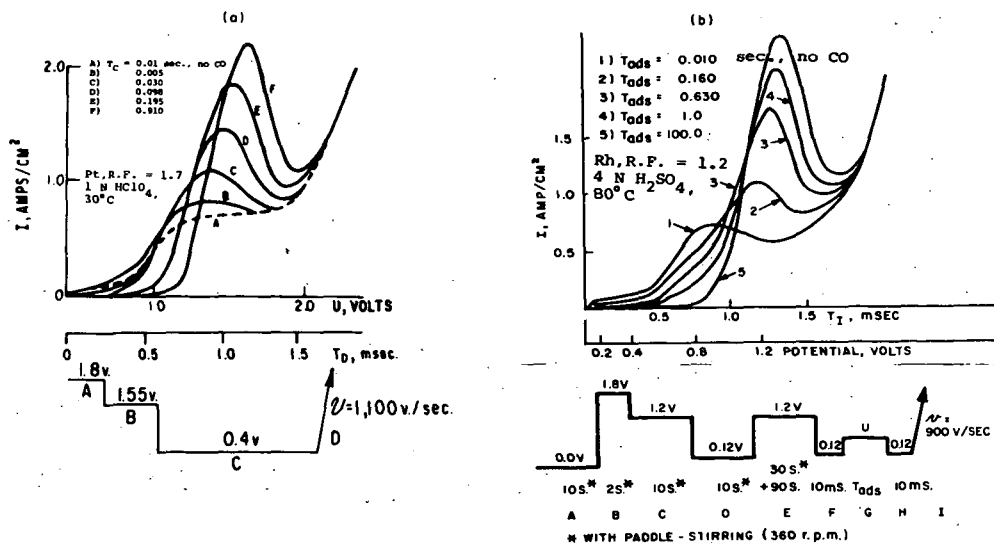
Figure 3. Determination of CO adsorption on Pt and Rh electrodes by anodic stripping. Steps C and G are adsorption steps in Figures 3a and 3b, respectively. The traces are measured during sweeps D and I in Figures 3a and 3b, respectively. All other steps are for pretreatment. (Figure 3a from Ref. 2; Figure 3b from Ref. 5).
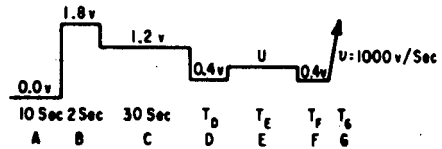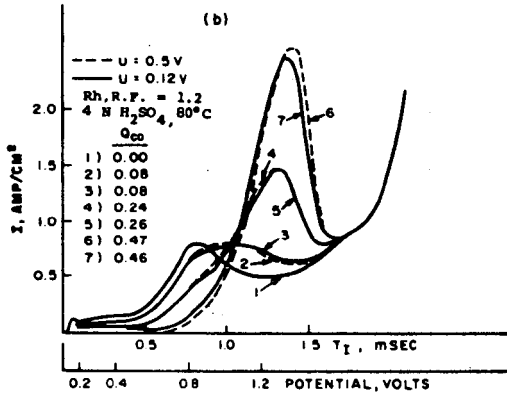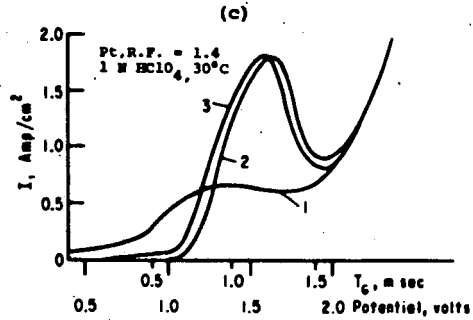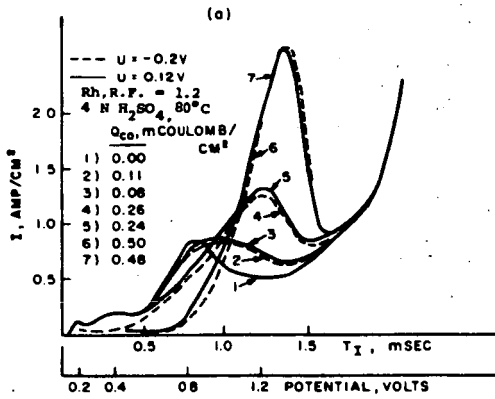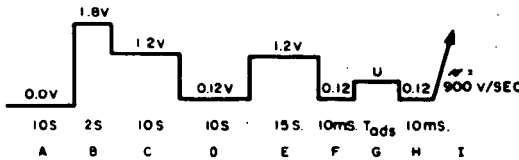
Figure 4. Effect of electrode potential at which CO is absorbed upon the trace corresponding to anodic stripping of adsorbed CO. Adsorption on Rh and on Pt occurs during steps G and E of the respective sequences. Comparisons of the traces obtained at the different potentials is made at almost identical values of the surface coverage (as measured by Q_{CO}). (Figures 4a and 4b from Ref. 5; Figure 4c from Ref. 4).
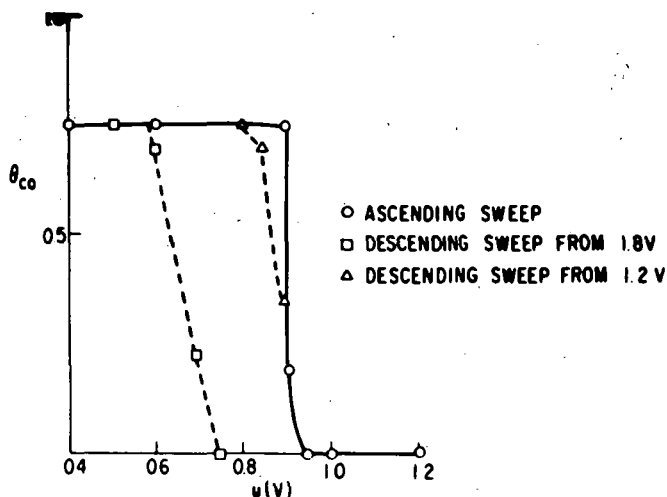
Figure 5. Coverage of a Pt electrode surface with CO. The 1 N HClO$_4$ was saturated with CO at 30°C and the solution was paddle-stirred throughout the experiment (360 rpm). The electrode potential was varied according to a triangular voltage-time sweep of speed 0.04 v./sec. θ_{CO} was defined relative to a hydrogen monolayer. The maximum value of θ_{CO} is equivalent to Q_{CO} (CO anodic stripping charge) of 8.28 mcoul. per cm of "true" (hydrogen) area. (After Ref. 1).
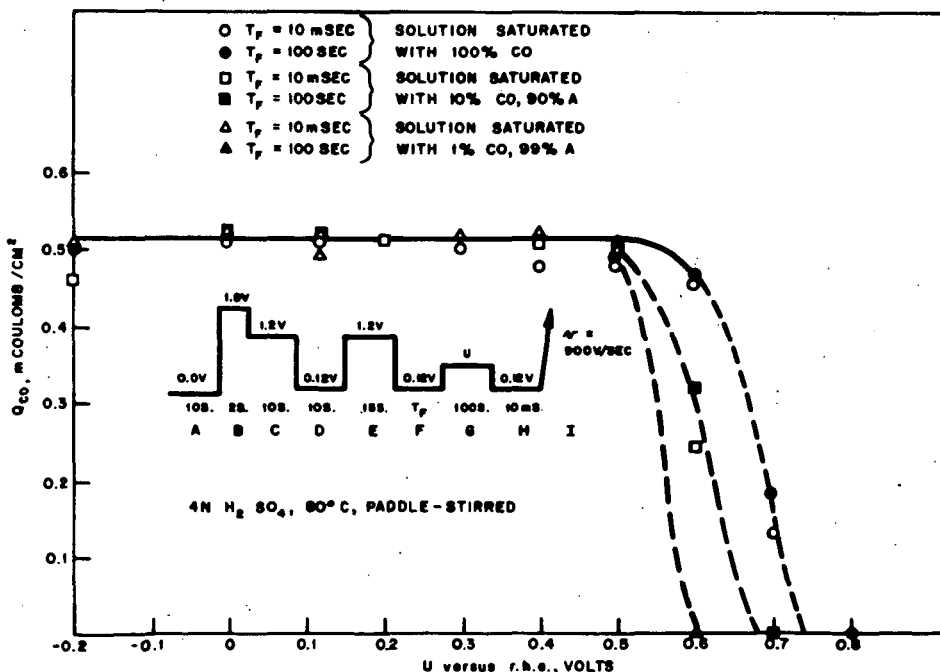

Figure 6. Coverage of a Rh electrode surface with CO. The 4 N H$_2$SO$_4$ was saturated with CO at 80°C, and Q_{CO} (charge required for anodic stripping of CO) was determined after adsorption at potential U of the indicated sequence. Q_{CO} is reported on the basis of geometric area and may be converted to "true" (hydrogen area) by dividing by the roughness factor of 1.16. (After Ref. 5)
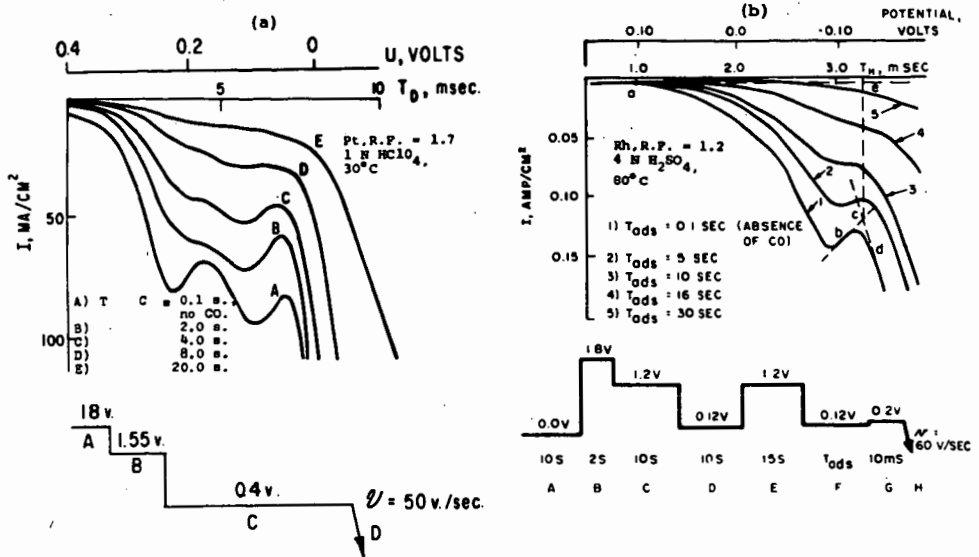
Figure 7. Determination of hydrogen co-deposition on electrodes partially covered with CO. The adsorption of CO occurs during steps C and F of Figures 7a and 7b, respectively. The traces correspond to hydrogen adsorption during sweeps D and H of Figure 7a and 7b, respectively. All other steps are for electrode pretreatment. (Figure 7a after Ref. 2; Figure 7b after Ref. 5).
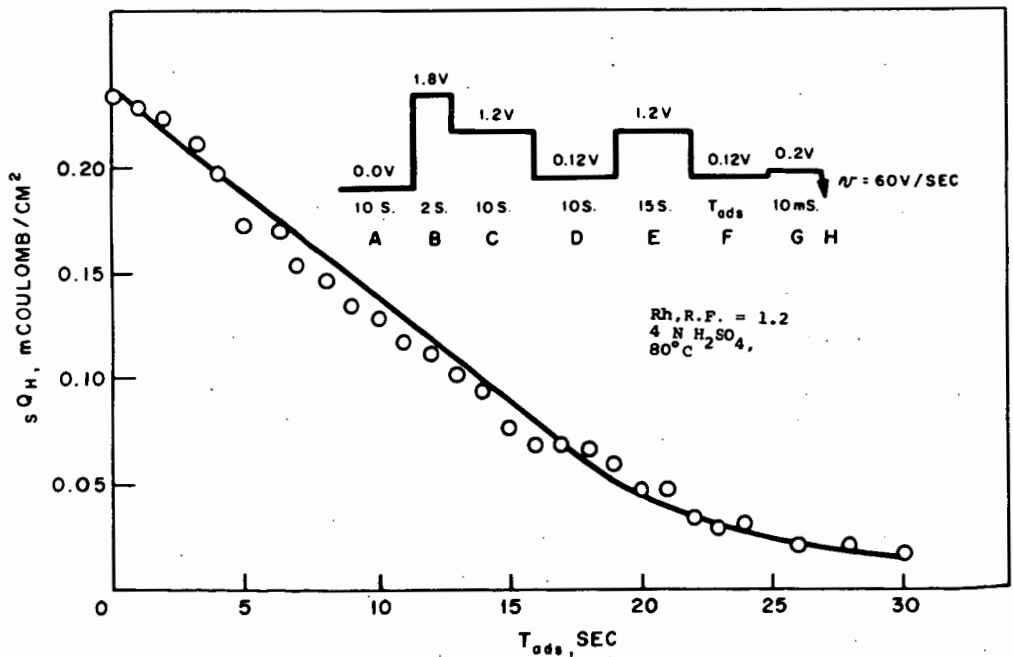

Figure 8. Variation of $_SQ_H$ (charge corresponding to saturation coverage with CO) with the time of adsorption of CO. The data was derived from traces such as those of Figure 7. (After Ref. 5)
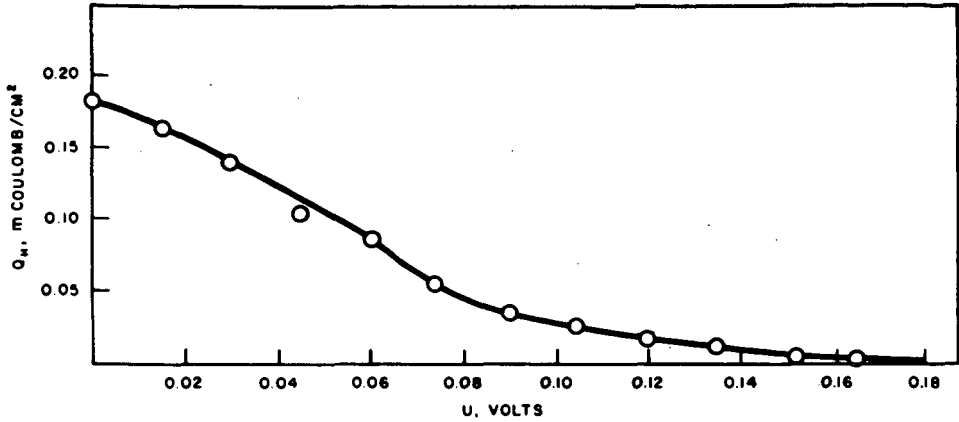
Figure 9. Equilibrium hydrogen coverage on a clean smooth Rh electrode (R.F. = 1.2, 4 N H_2SO_4 80°C). The coverage is expressed in terms of the equivalent charge, Q_H, for deposition or dissolution of the atomic hydrogen.
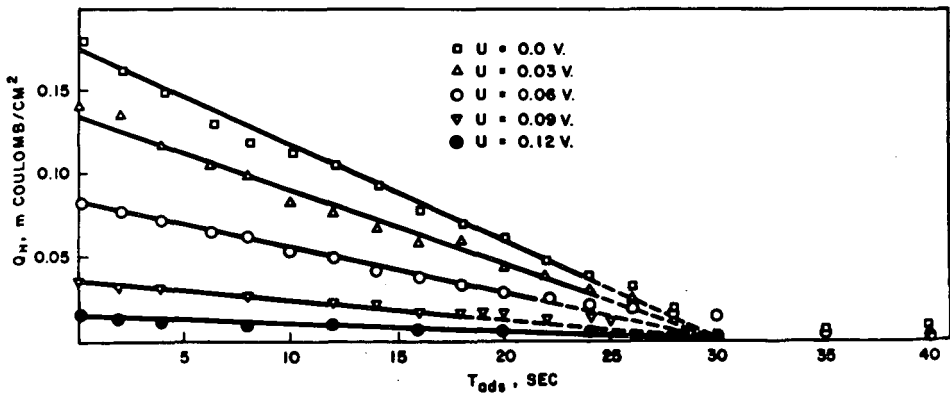

Figure 10. Decrease of equilibrium hydrogen coverage with time of adsorption of CO (4 N H_2SO_4 saturated with a gas mixture of 1% CO, 99% argon at 80°C; solution stirred). The coverage with hydrogen is expressed as the equivalent charge, Q_H, for deposition or dissolution of the atomic hydrogen.